

# ***In situ* reflection electron energy loss spectroscopy measurements of low temperature surface cleaning for Si molecular beam epitaxy**

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*In situ* analysis of hydrocarbon desorption from hydrogen terminated Si(100) surfaces was performed in a silicon molecular beam epitaxy system, using reflection electron energy loss spectroscopy, in conjunction with conventional reflection high energy electron diffraction analysis. Measurements of C *K* edge core loss intensities demonstrate that this method is sufficiently sensitive to enable *in situ* analysis of hydrocarbon desorption at fractional monolayer coverages during low-temperature isothermal anneals. Hydrocarbon desorption was found to begin at 115 °C, and at 200 °C complete desorption occurred within 10 min. Hydrocarbon coverage was not measurably affected by operation of ionization gauge filaments during low temperature anneals, but was increased by transient outgassing of the sample holder, and its environs.

Low-temperature epitaxial growth capability on Si surfaces is important to many aspects of device and integrated circuit technology. Fabrication of structures with abrupt doping profiles, heterojunctions,<sup>1</sup> metastable alloys, and growth on preprocessed very large scale integrated (VLSI) circuits<sup>2</sup> dictates that growth and processing temperatures be kept as low as possible. Such exacting requirements also have a significant impact on surface cleaning and treatment prior to epitaxial growth, and are incompatible with standard cleaning techniques based on native oxide desorption from silicon at temperatures above ~800 °C. This has motivated development of cleaning procedures that inhibit oxide formation by silicon surface passivation with a hydrogen termination. Almost inevitably, some physisorbed hydrocarbons remain on the silicon surface following hydrogen termination, and removal of these adsorbates is a key step in rendering a surface suitable for growth. Most processes for hydrogen termination involve surface exposure to a liquid or gaseous hydrofluoric acid solution. A comprehensive study of oxygen and carbon coverage on Si surfaces treated by a spin coating in an HF/ethanol solution in a nitrogen ambient<sup>3</sup> indicated gradual hydrocarbon desorption at 200 °C. Rapid sample heating to the growth temperature (400–450 °C) caused formation of silicon carbide, which is not removable at low temperatures. Subsequent successful epitaxial growth at 400 °C provided a critical test of hydrocarbon desorption during the 200 °C prebake. More recently, it was shown that a simple sample cleaning procedure consisting of chemical oxidation, followed by immersion in an aqueous HF solution prior to the 200 °C prebake is sufficient for epitaxial growth at 370 °C.<sup>4</sup> Another surface analysis study of adsorption of various hydrocarbon types to HF-treated silicon surfaces followed by device growth on these surfaces has shown that semiconductor device quality is a strong function of growth and characterization environments.<sup>5</sup>

Ideally, hydrocarbon desorption would be verified by *in situ* analysis in the growth chamber immediately prior to growth. In this letter, we report the first quantitative measurements of hydrocarbon desorption from hydrogen-

terminated Si(100) surfaces in a conventional molecular beam epitaxy (MBE) system with an *in situ* analysis technique, reflection electron energy loss spectroscopy (REELS).<sup>6,7</sup> REELS is a powerful technique with long working distance which does not compromise the growth environment in a molecular beam epitaxy system, and which can yield compositional information with depth resolution and absolute detection limits which are comparable to those of x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The *in situ* quantitative measurements of hydrocarbon desorption for silicon surfaces mounted on a molecular beam epitaxy sample manipulator (ISA RIBER type) during different stages of *in situ* sample preparation for MBE growth are described here. This configuration allows the onset of hydrocarbon desorption to be determined, and allows direct, time-resolved measurements of contamination unique to the growth chamber.

The typical experimental configuration for REELS has been described elsewhere.<sup>6–8</sup> Briefly, electrons from a 30 keV gun are scattered from the sample in the usual grazing incidence reflection high energy electron diffraction (RHEED) geometry, pass through a small aperture on the RHEED screen and are energy analyzed by a magnetic spectrometer. At 30 keV, electrons are strongly forward scattered<sup>6</sup> which eliminates the requirement for positioning the spectrometer close to the sample (unlike XPS and AES). In these measurements, simultaneous RHEED and REELS data are obtained which detect surface morphology, crystallinity, and chemical composition. Typical parameters for the gun in the measurements in this letter are 30 keV with 50  $\mu$ A emission current and about 0.5–2  $\mu$ A of sample current. The electron beam spot size on the sample was approximately 0.02 cm  $\times$  2 cm, yielding a sample current density of approximately 25  $\mu$ A/cm<sup>2</sup> and typical measurement times were 600–1000 s. The surface sensitivity of REELS is dependent on the incident angle of the electron beam and most of the measurements in this letter were performed with an incident beam angle of 5–10 mrad (0.5°).

Although the core electron ionization cross sections, and thus the measured core loss intensities, of low atomic number elements ( $Z=1-15$ ) are relatively large, these features are superimposed in an electron energy loss spectrum onto an exponentially decaying low loss background (due primarily to plasmon excitation). In order to quantify low levels of C coverage, on an H-terminated Si wafer, simple background subtraction<sup>9</sup> of the raw data is not appropriate. For these measurements, a standard second difference technique was used to extract the signal from the background in the energy loss spectrum.<sup>10</sup> A reference sample consisting of a 1  $\mu\text{m}$  epitaxial film of SiC grown on Si(100), whose surface stoichiometry was independently measured by x-ray photoelectron spectroscopy measurements, was used to determine empirical C  $K$  (285 eV) and Si  $L_{2,3}$  (99 eV) energy loss cross sections. Second difference C  $K$  energy loss spectra of the SiC sample were thus used as a reference for quantification of the C  $K$  intensity from adsorbed hydrocarbons on hydrogen-terminated Si wafers.<sup>11</sup>

Si(100) samples were prepared by alternate chemical formation and removal of a surface oxide (the RCA cleaning). An oxide is formed in an 80 °C 5:1:1 solution of  $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$  followed by a dip in a 1:10 solution of 48%  $\text{HF}:\text{H}_2\text{O}$ . The final step was to dip the Si wafer in the  $\text{HF}/\text{H}_2\text{O}$  solution to form a hydrogen terminated Si(100) surface. To control the nature of the hydrocarbon contamination, some of the samples were also rinsed with methanol after the immersion in the HF solution. The samples were immediately inserted into the MBE loadlock region and were transferred into the ultrahigh vacuum (UHV) growth chamber within 20–30 min of the final HF dip. The variation of C coverage on Si(100) surfaces with time was measured using *in situ* REELS. REELS data were first taken at room temperature. Subsequent data were collected at the prebake temperature (100–200 °C) at approximately 8 min intervals. After ten or twelve measurements at the prebake temperature, the wafer temperature was ramped at a rate of 12 °C per minute until  $(2\times 1)$  reconstruction of the Si(100) was observed (400–430 °C) using RHEED. REELS spectra were taken of the reconstructed surface and the C coverage was estimated. To minimize the effect of possible beam damage on the measurement, a new position on the sample was used for each subsequent measurement. In this case, nonuniform hydrocarbon coverage introduces a measurement error. To assess the degree of C coverage nonuniformity, REELS measurements were performed at room temperature on ten spots (each 2 mm apart) on a wafer. Figure 1 illustrates the variation of C coverage with position on the wafer and indicates that the coverage varies by about 1.3% of a monolayer with measurement position.

Figure 2 illustrates the time variation of C coverage during isothermal REELS measurements at three different temperatures. In Fig. 2(a), a gradual reduction of C coverage is observed during the first 30 min at 115 °C. The C coverage falls rapidly to below our detection limit during the first 10 min at 150 and 200 °C, but an increase in C coverage is observable at later times ( $\sim 50$  min). This rise

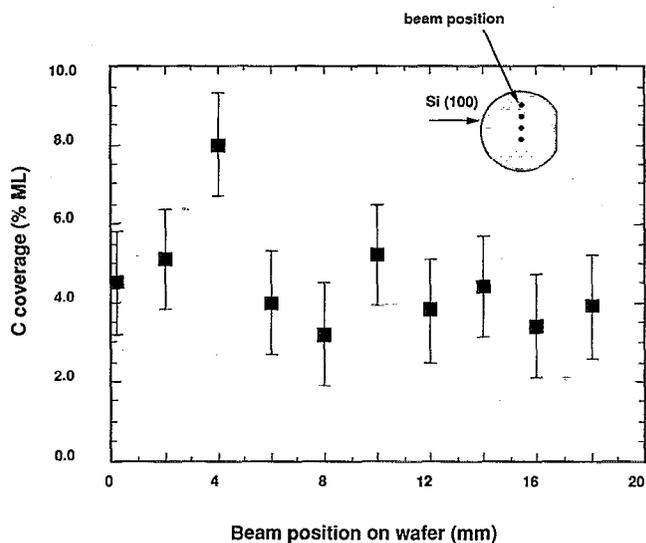


FIG. 1. Map of C coverage on a 2-in. cleaned Si(100) wafer which wafer was dipped in methanol following a RCA clean and an HF dip. REELS spectra were taken at room temperature to estimate the C coverage uniformity on the sample. The wafer was vertically translated 2 mm in each step to probe a new area on the wafer. The variation of C coverage along this wafer is within 1.3% of a monolayer.

in the hydrocarbon coverage is most likely due to outgassing of components in the UHV chamber which are unavoidably heated during the sample prebake (e.g., substrate holder). Notably, for samples prebaked at all the three temperatures in Figs. 2(a)–2(c), the C concentration at 400 °C is again negligible. Figure 2(d) is a set of typical second difference spectra at various temperatures. Previous studies indicate that for temperatures between 200 and 400 °C, the surface hydrogen coverage of an HF-dipped Si(100) surface evolves continuously from a mostly dihydride termination to a monohydride termination.<sup>12,13</sup> This is accompanied by a change in the surface reconstruction from  $(1\times 1)$  to  $(2\times 1)$ . This would suggest that during thermal annealing at temperatures between 200 and 400 °C, the fraction of hydrocarbon coverage which was adsorbed *in situ* was adsorbed on a silicon surface with a mixture of dihydride and monohydride termination, but desorbed if the sample temperature is ramped slowly, as previously suggested.<sup>3</sup>

It is difficult to generalize about hydrocarbon desorption mechanisms since these are in principle dependent on hydrocarbon structure and molecular weight, and since the relative abundance of different species depends on the cleaning and growth environments and cleaning solutions. Some observations can be made about hydrocarbon desorption from hydrogen-terminated Si surfaces by quantifying time-dependent coverages. The apparent activation energy for hydrocarbon desorption in our experiments of 0.03 eV, is much smaller than the energy required to break chemical bonds between C and Si, or H and Si, confirming that the hydrocarbons are physisorbed on the Si surface.

Although we had taken precautions in our measurements to minimize electron beam-induced damage on the H-terminated surfaces, we made independent measure-

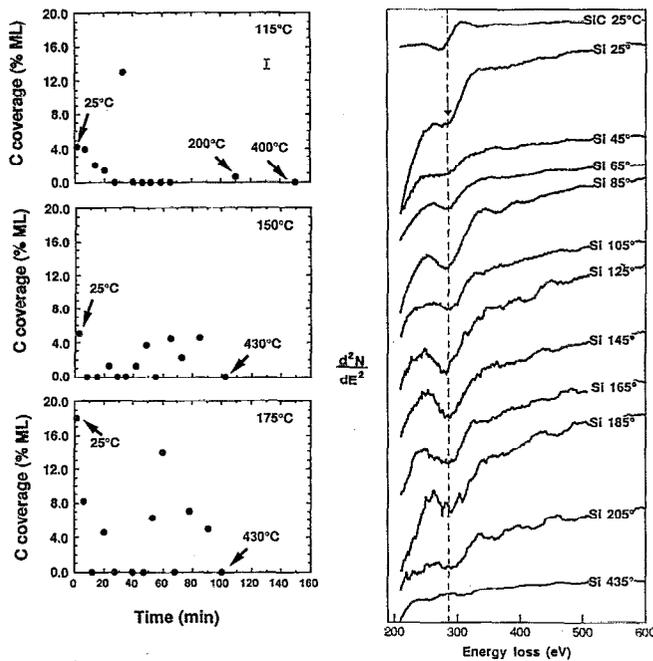


FIG. 2. (a)–(c) Isothermal measurements of C coverage at 115, 150, and 175 °C, respectively. The wafer prebaked at 115 °C was rinsed in methanol, following the HF immersion. The C coverage at room temperature gradually drops to zero within 30 min at 115 °C, whereas for 150 and 175 °C, the decline is sharp and in the first 10 min. Since according to the first plot, the desorption of hydrocarbons is activated at 115 °C, the desorption of the hydrocarbons is complete by the time wafer temperature has reached 150 or 175 °C. A  $2\times 1$  reconstruction RHEED pattern is observed at 400–430 °C. The intermediate rise in the C coverage in the bottom two plots is attributed to outgassing from the unbaked surfaces (e.g., substrate block in the chamber). The final C coverage at 400 °C is again negligible. (d) shows variation of typical second difference C 1s spectra with temperature from the Si(100) surface. The SiC data is used as a reference and the arrow indicates the onset of the C K ionization edge at 284 eV.

ments to assess the degree of beam influence on the H—Si bond. Consecutive REELS measurements of C coverages were made for the same point on Si wafers at room temperature with a 30 keV electron beam and  $0.03 \text{ mA/cm}^2$  sample current density. No change in C surface coverage was observed after 20–50 min of irradiation. This finding is consistent with recent Auger studies<sup>14</sup> of time evolution profiles of O and C on H-terminated Si(100) surfaces, which reported an incubation time before C and O are detected on the Si(100) surface which increases with increasing beam energy. Our beam current density is lower than that work, and our irradiation times are lower by factors of 2 or 3. Also, it was reported that the cross section of hydrogen desorption decreases by orders of magnitude with increasing electron energy. Given our higher incident electron energy of 30 keV (as opposed to 2–5 keV used in Auger measurements), and shorter irradiation times, it is not surprising that we do not observe significant beam-induced hydrocarbon desorption.

It is natural to suspect that hydrocarbon dissociation by hot filaments, such as an ionization gauge filament, is responsible for the contamination of the sample surface. So

far, this has been suggested<sup>4</sup> due to the quality of the epitaxial films grown. However, to separate this effect from other factors which could affect growth, we measured C coverage with the ionization gauge, which is in a line of sight to the substrate, on and off. The variation in the C coverage in these measurements were comparable to the spatial fluctuation in hydrocarbon coverage indicated in Fig. 1 and the coverages in the two cases were similar. These measurements indicate that the ionization gauge operation does not have a significant effect on the hydrocarbon adsorption.

We have performed *in situ* measurements of C coverage of RCA-cleaned and HF-dipped Si(100) surfaces in a molecular beam epitaxy growth chamber. We observed that hydrocarbon desorption is activated at 115 °C and with the sensitivity of our measurements the coverage gradually drops to negligible levels after 30 min. At the temperature that ( $2\times 1$ ) reconstruction is observed in RHEED, C coverage is negligible provided that the sample is annealed at  $\sim 115\text{--}200$  °C before heating to high temperature. We have demonstrated that the sensitivity of the REELS technique is sufficient to detect hydrocarbon coverages of  $\sim 1\%$  of a monolayer and since lower electron doses can be employed, REELS is a somewhat less destructive technique than Auger electron spectroscopy.

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